



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : **Confirmation No. 7447**  
Hisashi ISAKA : Docket No. 2002-0217A  
Serial No. 10/067, 369 : Group Art Unit 1712  
Filed February 7, 2002 : Examiner Robert E. Sellers  
CURING COMPOSITION

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**DECLARATION**

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Akiko KOJIMA, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the  
Japanese Priority Application No. 2001-66440, filed March 9, 2001.

I further declare that all statements made herein of my own knowledge are true  
and that all statements made on information and belief are believed to be true; and  
further that these statements were made with the knowledge that willful false  
statements and the like so made are punishable by fine or imprisonment, or both,  
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statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 19th day of March, 2004.

*Akiko Kojima*

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Akiko KOJIMA

(TRANSLATION)

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: March 9, 2001

Application Number: Patent Application No. 2001-66440

[ ST.10/C]: [JP2001-66440]

Applicant(s): Kansai Paint Co., Ltd.

March 1, 2002

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Kozo OIKAWA

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Commissioner,  
Japan Patent Office

Certification No. 2002-3012022



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[Document Name] Patent Application

[Reference Number] 10370

[Submitted to] Commissioner, Patent Office

[International Classification] C09D163/00

[Inventor]

[Address] c/o Kansai Paint Co., Ltd., 17-1, Higashiyawata 4-chome,  
Hiratsuka-shi, Kanagawa-ken

[Name] Hisashi ISAKA

[Applicant]

[Identification Number] 000001409

[Name] Kansai Paint Co., Ltd.

[Representative] Tamotsu SHIRAIWA

[Priority Claim Based on Prior Application]

[Application Number] Patent Application No. 2001-31763

[Date of Filing] February 8, 2000

[Indication of Official Fees]

[Number of Prepayment] 000550

[Amount of Payment] 21000

[List of Submitted Objects]

[Name of Object] Specification 1

[Name of Object] Abstract 1

[Proofing] Required

[Document Name] Specification

[Title of the Invention] Method for Forming a Cured Coating Film

[Claims]

[Claim 1] A method for forming a cured coating film, characterized by applying, on an uncured thermosetting colored layer, a curing composition comprising:

5 (A) a polymerizable cyclic structure-containing component comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one polymerizable cyclic structure in a molecule and

(B) 0.01 to 2 parts by weight of a metal triflate per 100 parts by  
10 weight of the above component (A), wherein the above polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average and then baking it .

15 [Claim 2] The method for forming a cured coating film as set forth in Claim 1, wherein a metal in the metal triflate (B) is at least one metal selected from scandium, yttrium, lanthanoid series metals, actinoid series metals, magnesium, and zinc.

[Claim 3] The method for forming a cured coating film as set forth in Claim 1 or  
20 2, wherein the colored layer is formed by applying a water-based coating composition.

[Claim 4] The method for forming a cured coating film as set forth in any of Claims 1 to 3, wherein the colored layer is formed on a car body.

[Detailed Description of the Invention]

25 [0001]

[Technical field to which the invention belongs]

The present invention relates to a method for forming a cured coating film which is excellent in characteristics such as a hardness and a finish.

[0002]

30 [Prior art and its problem]

A curing composition comprising an epoxy group-containing resin and a cationic polymerization catalyst has so far been known, and a coating

composition comprising a specific epoxy group-containing resin and a heat latent cationic polymerization catalyst is disclosed in, for example, Japanese Patent Application Laid-Open No. 158580/1998. However, this composition involves the problems that it is liable to be influenced by humidity, so that the coating environment and the coating steps are restricted to a large extent.

5 [0003]

Also, known is a method in which cyclic ethers represented by an epoxy compound are subjected to ring-opening polymerization in a vessel using a Lewis acid and an onium salt as initiators to synthesize polyethers. Various initiators are researched in this polyether synthesis field, and disclosed in, for example, Japanese Patent Application Laid-Open No. 502531/1996 is a method in which cyclic ethers are subjected to polymerization using a metal triflate, which is a Lewis acid, to synthesize polyethers.

10 [0004]

Further, it is described in U.S. Patent No. 3,842,019 and Polymer, Vol. 41, p. 8465 to 8474, 2000 that a cured matter is obtained by combining a multifunctional epoxy compound with a metal triflate.

15 [0005]

An object of the present invention is to provide a method for forming a coating film which is less liable to be influenced by coating environment and coating conditions in a wet-on-wet coating step capable of shortening working steps and can provide a cured coating film excellent in curing property at a relatively low curing temperature without using a lot of a polymerization catalyst and excellent in hardness and finish.

20 [0006]

[Means to solve the problems]

25

Intensive researches repeated by the present inventors in order to achieve the object described above have resulted in finding that a curing composition having a good hardness and finish can be formed by using a specific metal triflate which is a Lewis acid as a cationic polymerization catalyst for a polymerizable cyclic structure-containing component and applying it on an uncured thermosetting colored layer, and they have come to complete the present invention.

30

[0007]

That is, the present invention provides a method for coating a cured coating film, characterized by applying, on uncured thermosetting colored layer, a curing composition comprising:

5 (A) a polymerizable cyclic structure-containing component comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one polymerizable cyclic structure in a molecule and

(B) 0.01 to 2 parts by weight of a metal triflate per 100 parts by  
10 weight of the above component (A),  
wherein the above polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average and then baking it.

15 [0008]

The method for forming a cured coating film of the present invention shall be explained below in detail.

[0009]

[Mode for carrying out the invention]

20 At first, a curing composition of the present invention shall be explained below in detail.

The curing composition in the present invention comprises the polymerizable cyclic structure-containing component (A) and the metal triflate (B) each described below as essential components.

25 [0010]

Polymerizable cyclic structure-containing component (A)

The polymerizable cyclic structure-containing component (A) in the curing composition used in the method of the present invention comprises a compound (a-1) having at least two polymerizable cyclic ether structures in a  
30 molecule or is a mixture of the above compound (a-1) and a compound (a-2) having one polymerizable cyclic structure in a molecule.

[0011]

A compound having the polymerizable cyclic ether structure in the

above compound (a-1) includes oxiranes, oxetanes, oxolanes, oxepanes, and a cyclic formal such as dioxolanes and trioxanes, which have at least two polymerizable cyclic ether structures in a molecule.

[0012]

5 Further, capable of being given as the polymerizable cyclic structure in the above compound (a-2) are cyclic ethers including oxiranes, oxetanes, oxolanes, oxepanes, and a cyclic formal such as dioxolanes and trioxanes, and in addition thereto, cyclic esters (lactone), cyclic amides (lactam), and cyclic iminoethers, which have one polymerizable cyclic structure in a molecule.

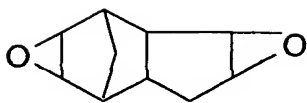
10 [0013]

A compound in which a cyclic ether structure equivalent falls in a range of 70 to 3,000, preferably 80 to 1,500 is suitably used as the compound (a-1) described above.

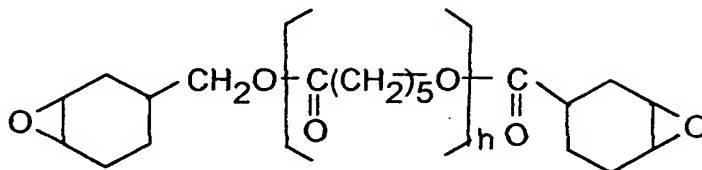
[0014]

15 Among the compounds (a-1), capable of being given as the oxiranes are, for example, compounds having two or more epoxy groups such as dicyclopentadiene dioxide,  
(3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexanecarboxylate,  
bis(2,3-epoxycyclopentyl) ether, bis(3,4-epoxycyclohexylmethyl) adipate,  
20 bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate,  
(3,4-epoxy-6-methylcyclohexyl)methyl-3,4-epoxy-6-methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl) acetal,  
bis(3,4-epoxycyclohexyl) ether of ethylene glycol,  
3,4-epoxycyclohexanecarboxylic acid diester of ethylene glycol,  
25 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane,  
Celoxide 2080 (trade name, difunctional epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), Epolead GT300 (trade name, trifunctional alicyclic epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), Epolead GT400 (trade name, tetrafunctional alicyclic epoxy resin, manufactured by Daicel  
30 Chemical Industries, Ltd.), Celoxide 3000 (trade name, difunctional epoxy compound, manufactured by Daicel Chemical Industries, Ltd.), EHPE (trade name, multifunctional epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), compounds represented by the following formulas:

[0015]

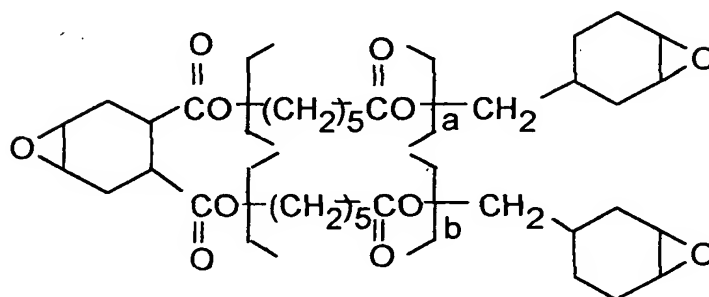


5



10

(h is an integer of 1 or more)

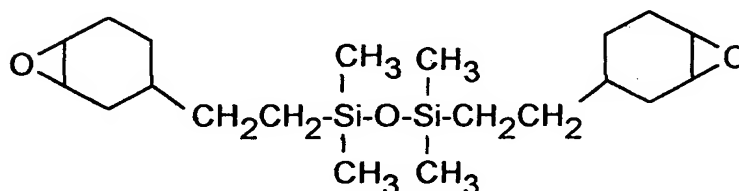


15

(a and b are an integer of 0 or more)

[0016]

20



[0017]

25

ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin diglycidyl ether, polyglycerin polyglycidyl ether, trimethylolpropane polyglycidyl ether, pentaerythritol polyglycidyl ether, spiro glycol diglycidyl ether, 30 2,6-diglycidyl phenyl ether, sorbitol polyglycidyl ether, triglycidyl isocyanurate, bisphenol A diglycidyl ether, butadiene dioxide, diglycidyl phthalate, diglycidyl tetrahydrophthalate, vinylcyclohexene dioxide, limonene dioxide, bisphenol A epoxy resins, cresol novolak epoxy resins, and epoxyphenol novolak resins;

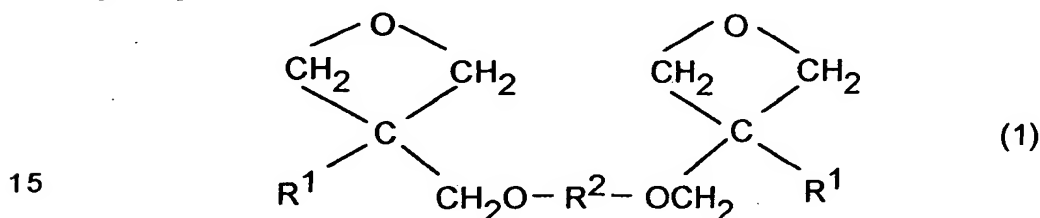


polymers of epoxy group-containing polymerizable unsaturated monomers such as glycidyl (meth)acrylate, methylglycidyl (meth)acrylate, allyl glycidyl ether, 3,4-epoxycyclohexylmethyl (meth)acrylate, caprolactone-modified compounds of 3,4-epoxy-cyclohexylmethyl (meth)acrylate, and 3,4-epoxyvinylcyclohexane;  
 5 and copolymers of the above epoxy group-containing polymerizable unsaturated monomers with other copolymerizable monomers. In the present invention, "(meth)acrylate" means acrylate or methacrylate.

[0018]

Among the compounds (a-1), capable of being given as the oxetanes  
 10 is, for example, a compound represented by the following formula (1):

[0019]



[0020]

(In the above formula, two R<sup>1</sup>'s may be the same or different and mean the same as described previously; and R<sup>2</sup> represents an alkylene group having 1 to  
 20 6 carbon atoms, a cycloalkylene group, a phenylene group, a xylylene group, or a polyalkyleneoxy group having 4 to 30 carbon atoms.)

[0021]

Among the compounds (a-1), capable of being given as the compound having both oxiranes and oxetanes are  
 25 3-ethyl-3-(3,4-epoxycyclohexylmethyl)oxymethyloxetane and 3-ethyl-3-glycidyloxymethyloxetane.

[0022]

Capable of being suitably used as the compound (a-2) having one polymerizable cyclic structure in a molecule is a compound in which a  
 30 polymerizable cyclic structure equivalent falls in a range of 70 to 1,000, preferably 80 to 500.

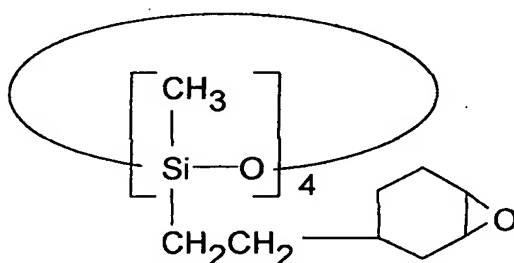
[0023]

Among the compounds (a-2), capable of being given as the cyclic

ethers are, for example, oxiranes such as glycidol, styrene oxide, alkyl monoepoxide, phenyl glycidyl ether, alkyl monoglycidyl ether, Cardura E10 (trade name, manufactured by Shell Chemicals), Glydex N10 (trade name, manufactured by Exxon Co., Ltd.), alkyl glycidyl esters including Araldite PT910 (trade name, manufactured by Ciba-Geigy Co., Ltd.), glycidyl (meth)acrylate, methylglycidyl (meth)acrylate, allyl glycidyl ether, 3,4-epoxycyclohexylmethyl (meth)acrylate, caprolactone-modified products of 3,4-epoxycyclohexylmethyl (meth)acrylate, 3,4-epoxyvinylcyclohexane, cyclohexene oxide,  $\alpha$ -pinene oxide, (3,4-epoxycyclohexyl)methyl alcohol, (3,4-epoxycyclohexyl)ethyltrimethoxysilane, and compounds represented by the following formula:

[0024]

15



20 [0025]

oxetanes such as 3-ethyl-3-methoxymethyloxetane, 3-ethyl-3-ethoxymethyloxetane, 3-ethyl-3-butoxymethyloxetane, 3-ethyl-3-hexyloxymethyloxetane, 3-methyl-3-hydroxymethyloxetane, 3-ethyl-3-hydroxymethyloxetane, 3-ethyl-3-allyloxymethyloxetane, 3-ethyl-3-(2'-hydroxyethyl)oxymethyloxetane, 3-ethyl-3-(2'-hydroxy-3'-phenoxypropyl)oxymethyloxetane, 3-ethyl-3-(2'-hydroxy-3'-butoxypropyl)oxymethyloxetane, 3-ethyl-3-(2'-butoxyethyl)oxymethyloxetane, 3-ethyl-3-benzyloxymethyloxetane, 3-ethyl-3-(p-tert-butylbenzyloxymethyl)oxetane, 3-ethyl-3-methacryloyloxymethyloxetane, and 3-ethyl-3-acryloyloxymethyloxetane; oxolanes such as tetrahydrofuran and tetrahydrofurfuryl alcohol; oxepanes such as oxepane; dioxoranes such as 1,3-dioxorane; and trioxoranes such as 1,3,5-trioxorane.

[0026]

The cyclic esters (lactone) include  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, enanthlactone, 3-methyl- $\beta$ -propiolactone, 3-methyl- $\gamma$ -butyrolactone, 3-methyl- $\delta$ -valerolactone, 3-methyl- $\epsilon$ -caprolactone, 4-methyl- $\epsilon$ -caprolactone, and 3,3,5-trimethyl- $\epsilon$ -caprolactone.

[0027]

The cyclic amide (lactam) includes azetidinone, pyrrolidone, and  $\epsilon$ -caprolactam.

The cyclic iminoethers include oxazoline and oxazine.

10 [0028]

These compounds having a polymerizable cyclic structure can be used alone or in combination of two or more kinds thereof.

[0029]

The polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000, particularly 120 to 700 on average. The blending proportions of the compound (a-1) and the compound (a-2) each described above in the polymerizable cyclic structure-containing component (A) are preferably in the following ranges based on 100 parts by weight of the total of the both compounds from the viewpoint of a curing property:

Compound (a-1): 20 to 100 parts by weight, preferably 40 to 100 parts by weight

Compound (a-2): 0 to 80 parts by weight, preferably 0 to 60 parts by weight

[0030]

#### Metal triflate (B)

A metal triflate which is the (B) component of the curing composition in the method of the present invention functions as a cationic polymerization catalyst for the polymerizable cyclic structure-containing component (A) and is a trifluoromethanesulfonic acid metal salt. As described above, it is known that a polymerizable cyclic structure-containing compound can be polymerized and three-dimensionally cross-linked by using a metal triflate as a cationic

polymerization catalyst.

[0031]

A metal triflate is known as a Lewis acid which is relatively stable in water, and it is known as well that metals of particularly the 3 group in the periodic table and specific metals are stable in water (refer to O. Kobayashi, J. Am. Chem. Soc., 120, p. 8287 to 8288, 1998).

[0032]

At least one metal selected from metals of the 3 group in the periodic table, magnesium, and zinc is suited as a metal of the metal triflate described above from the viewpoint of a curing property, coloring, and a pot life. The metal of the 3 group in the periodic table includes scandium, yttrium, lanthanoid series metals, and actinoid series metals. Among them, zinc is suited as the metal of the metal triflate.

[0033]

In the curing composition described above, the blending amount of the metal triflate (B) falls suitably in a range of 0.01 to 2 parts by weight, particularly 0.05 to 2 parts by weight per 100 parts by weight of the polymerizable cyclic structure-containing component (A) described above. When the amount is less than 0.01 part by weight, a curing property is insufficient, and when it exceeds 2 parts by weight, a coating film obtained from this cured composition is easily colored, so that they are not preferred.

[0034]

The curing composition used in the method of the present invention comprises as essential components, the polymerizable cyclic structure-containing component (A) and the metal triflate (B) each described above and can comprise, if necessary, an organic solvent, a reactive diluent, a pigment, a UV absorber, a surface controller, an antioxidant, a fluidity controller, and a wax.

[0035]

In the method of the present invention, the curing composition described above is applied on an uncured thermosetting colored layer (wet-on-wet coating) and then baked to cure the colored layer and the coating film layer of the above curing composition at the same time.

[0036]

To be specific, capable of being given are, for example, a 2-coating 1-baking method in which the curing composition described above is used as a coating composition for forming a clear layer to apply the above curing composition on an uncured thermosetting colored layer (wet-on-wet coating) and bake them, and a 3-coating 1-baking method in which the above curing compositions are applied in order (wet-on-wet coating) for a first colored layer, a second coating layer, and a clear layer to bake them at the same time. These methods are merely examples, and the uncured thermosetting colored layer described above regarding the 2-coating 1-baking method shall not be restricted to a coating layer and an ink layer. The method of the present invention includes any methods as long as the above curing composition is applied on the uncured (including semi-cured) colored layer and heated to cure. For example, if the colored layer may be formed by carrying out removal of water and a solvent and semi-curing at a pre-heating step usually carried out in a water-based coating material, it is not deviated from the category of the method of the present invention. Further, the uncured thermosetting colored layer may not be cured alone by itself and can be cured by transfer of a curing agent from a layer coated thereon.

20 [0037]

An important point in the method of the present invention is that it improved the following point: When a curing composition is applied on an uncured thermosetting colored layer by wet-on-wet, various effects are exerted on the layer of the curing composition by a solvent and the like (moisture and basic substances in the case of a water-based coating composition) contained in the colored layer which is a lower layer, and therefore, a cross-linking method of a curing composition coated thereon has so far been restricted. In particular, when a lower layer comprises a water-based color coating composition, a curing composition is reduced in curing property to a large extent due to deactivation of a catalyst, so that it has so far been difficult to cure it in a reaction of the curing composition making use of ionic polymerization. In the method of the present invention, however, in spite of the reaction of the curing composition making use of ionic polymerization described above, the curing

property is scarcely influenced by an uncured lower layer and the curing composition shows a good curing property even when a lower layer comprises a water-based color coating composition.

[0038]

5                In the method of the present invention, the focus is on a metal triflate being relatively stable in water, and the metal triflate is applied to the polymerizable cyclic structure-containing component (A) described above, whereby it has been found that a cationic polymerization is achieved as well in a wet-on-wet coating.

10        [0039]

              In the method of the present invention, a substrate on which a cured coating film is formed shall not specifically be restricted, and suited are materials such as car bodies, car parts, cans for beverages, parts for home electric appliances, and metal sheets.

15        [0040]

              In the method of the present invention, the curing composition can be applied on a colored layer, for example, by a method such as roll coating, curtain flow coating, and spray coating. When the curing composition is applied, the dried coating film thickness can suitably be selected in a range  
20        where the good coating film appearance and curing property are obtained, and it falls usually in a range of about 2 to 80  $\mu\text{m}$  in terms of a dried coating film thickness. It falls preferably in a range of usually about 2 to 20  $\mu\text{m}$  when used for coating cans and preferably about 15 to 80  $\mu\text{m}$  when used for coating car bodies. A desirable temperature for baking the colored layer and the curing  
25        composition layer after coating is in a range of 50 to 220°C.

[0041]

[Examples]

1. Preparation of a curing composition

Synthetic Example 1: synthesis of an oxirane-containing acrylic resin mixed  
30        solution (a-1)

              A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube, and a dropping funnel was charged with 650 parts of Celoxide 2021P (trade name, difunctional

epoxy compound, epoxy equivalent: about 130, manufactured by Daicel Chemical Industries, Ltd.). The reactor was substituted in an inside thereof with nitrogen, heated, and maintained at 165°C. Added drop by drop thereto in 4 hours was a mixture comprising 50 parts of styrene, 150 parts of n-butyl acrylate, 75 parts of 2-ethylhexyl acrylate, 75 parts of 2-hydroxyethyl acrylate, 150 parts of glycidyl methacrylate, and 50 parts of 2,2'-azobis(2-methylbutyronitrile). After finishing dropping, the solution was aged for 30 minutes, and the mixture of 2.5 parts of 2,2'-azobis(2-methylbutyronitrile) and 25 parts of Celoxide 2021P was further added drop by drop thereto in one hour. Then, the solution was aged for 30 minutes, whereby obtained was a mixed solution (a-1) of an acrylic resin and Celoxide 2021P having a non-volatile content of 100% and a Gardner viscosity (20°C) of X<sup>+</sup>. The acrylic resin contained in the resulting mixed solution (a-1) had a hydroxyl group value of 72 mg KOH/g, a number average molecular weight of 1510, and a weight average molecular weight of 2330.

[0042]

Synthetic Example 2: synthesis of an oxetane-containing acrylic resin mixed solution (a-2)

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube, and a dropping funnel was charged with 650 parts of Celoxide 2021P, and the reactor was substituted in an inside thereof with nitrogen, heated, and maintained at 165°C. Added drop by drop thereto in 4 hours was a mixture comprising 50 parts of styrene, 150 parts of n-butyl acrylate, 75 parts of 2-ethylhexyl acrylate, 75 parts of 2-hydroxyethyl acrylate, 150 parts of 3-ethyl-3-methacryloyloxymethyloxetane, and 50 parts of 2,2'-azobis(2-methylbutyronitrile). After finishing dropping, the solution was aged for 30 minutes, and the mixture of 2.5 parts of 2,2'-azobis(2-methylbutyronitrile) and 25 parts of Celoxide 2021P was further added drop by drop thereto in one hour. Then, the solution was aged for 30 minutes, whereby obtained was a mixed solution (a-2) of an acrylic resin and Celoxide 2021P having a non-volatile content of 100% and a Gardner viscosity (20°C) of Y. The acrylic resin contained in the resulting mixed solution (a-2) had a hydroxyl group value of 72 mg KOH/g, a number average molecular

weight of 1440, and a weight average molecular weight of 2190.

[0043]

Synthetic Example 3: synthesis of a hydroxyl group-containing compound (reactive diluent) (a-3)

5                   A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube, and a dropping funnel was charged with 296 parts of dimethylolbutanoic acid, and the reactor was substituted in an inside thereof with nitrogen and heated at 120°C. Added drop by drop thereto in 2 hours was 490 parts of "Cardura E10" (manufactured  
10 by Shell Chemicals), and the temperature was maintained at 120°C. When the acid value became 9 or less, the solution was cooled down to terminate the reaction. The resulting component (a-3) had a solid content of about 98% and a Gardner viscosity (20°C) of Z<sub>6</sub>Z<sub>7</sub>, and the solid matter had a hydroxyl group value of 428 mg KOH/g, a number average molecular weight of 600, and a  
15 weight average molecular weight of 610.

[0044]

Preparation of a curing composition

Preparation Example 1

20                   Mixed were 300 parts of Celoxide 2021P, 3 parts of zinc triflate, and 3 parts of propylene glycol monomethyl ether to prepare a curing composition (A-1).

[0045]

Preparation Examples 2 to 17

25                   Curing compositions (A-2) to (A-14) and (B-1) to (B-3) were prepared in the same manner as in Preparation Example 1, except that components shown in the following Table 1 were used. Curing compositions (B-1) to (B-3) obtained in Preparation Examples 15 to 17 are for comparing.

[0046]

30                   In Table 1, codes shown below mean the following:

Zn(OTf) <sub>2</sub>	: zinc triflate
Mg(OTf) <sub>2</sub>	: magnesium triflate
Yb(OTf) <sub>3</sub>	: ytterbium triflate
Gd(OTf) <sub>3</sub>	: gadolinium triflate



LiOtf : lithium triflate  
 AgOtf : silver triflate  
 50% CI-2639 : sulfonium salt base cationic polymerization  
 initiator (active ingredient: 50%, manufactured by  
 Nippon Soda Co., Ltd.)

5

Curing property of curing composition

The curing properties of the curing compositions obtained in the respective preparation examples described above were examined in the following manner.

10

The curing composition was applied on a tin plate by means of an applicator so that the cured film thickness was about 45  $\mu\text{m}$  and heated and dried at the respective temperatures of 100°C, 120°C, and 140°C for 30 minutes. It was left standing for 24 hours, and then, the coating film hardness was measured by means of a Knoop hardness meter. Then, the coating film was separated and extracted in acetone under reflux for 6 hours to determine a gel ratio (%) from the coating film weights before and after extraction according to the following equation:

15

20

$$\text{gel ratio (\%)} = \frac{\text{coating film weight after extraction}}{\text{coating film weight before extraction}} \times 100$$

Results thereof are shown in the following Table 1.

[0047]

[Table 1]

Table 1

Preparation Example No.		1	2	3	4	5	6	7	8	9
Kind of curing composition		A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
Celoxide 2021P		300	300	300	300	300	250	250	250	250
Acrylic resin solution (a-1)										
Acrylic resin solution (a-2)										
Cardura E-10										
3-Ethyl-3-hydroxy-methyloxetane										
$\epsilon$ -Caprolactone										
$\text{Zn}(\text{OTf})_2$		3	1.5				3			
$\text{Mg}(\text{OTf})_2$				3				3		
$\text{Yb}(\text{OTf})_3$					3				3	
$\text{Gd}(\text{OTf})_3$						3				3
$\text{LiOTf}$										
$\text{AgOTf}$										
50% CI-2639										
Compound (a-3)							50	50	50	50
Propylene glycol monomethyl ether		3	3	3	3	3	3	3	3	3
Gel ratio (%)	100°C baking	100	100	100	100	100	93	90	94	93
	120°C baking	99	100	100	99	100	95	93	95	95
	140°C baking	98	98	99	99	99	96	93	96	95
Knoop hardness	100°C baking	35	35	30	36	33	25	22	25	24
	120°C baking	36	35	34	34	36	30	28	28	30
	140°C baking	35	36	35	35	36	30	29	29	29

[0048]

[Table 2]

Table 1 (continued)

Preparation Example No.		10	11	12	13	14	15	16	17
Kind of curing composition		A-10	A-11	A-12	A-13	A-14	B-1	B-2	B-3
Celoxide 2021P				240	240	240	300	300	300
Mixed solution (a-1) obtained in Synthetic Example 1		300							
Mixed solution (a-2) obtained in Synthetic Example 2			300						
Cardura E-10				60					
3-Ethyl-3-hydroxy-methyloxetane					60				
ε-Caprolactone						60			
Zn(OTf) <sub>2</sub>		3	3	1.5	1.5	1.5			
Mg(OTf) <sub>2</sub>									
Yb(OTf) <sub>2</sub>									
Gd(OTf) <sub>2</sub>									
LiOTf							3		
AgOTf								3	
50% Cl-2639									6
Compound (a-3)									
Propylene glycol monomethyl ether		3	3	3	3	3	3	3	
Gel ratio (%)	100°C baking	95	96	100	100	99	0	100	0
	120°C baking	98	99	99	100	99	0	100	0
	140°C baking	99	100	97	99	99	0	99	0
Knoop hardness	100°C baking	18	20	16	17	10	—	35	—
	120°C baking	20	22	18	17	12	—	35	—
	140°C baking	21	23	19	18	12	—	36	—

[0049]

## 2. Preparation of coating composition for water-based colored base coat

## Synthetic Example 4: synthesis of an acrylic resin aqueous dispersion (c-1)

A reaction vessel was charged with 140 parts of deionized water, 2.5 parts of "Newcol 707SF" (trade name, surfactant, solid content: 30%, manufactured by Nippon Nyukazai Co., Ltd.), and 80 parts of the following monomer mixture (1). They were stirred and mixed in nitrogen flow, and a monomer emulsion comprising 4 parts of 3% ammonium persulfate and 42 parts of deionized water was added to the reaction vessel at 60°C in 4 hours by means of a constant flow pump. After finishing addition, the solution was aged for one hour.

## Monomer mixture (1)

	Methyl methacrylate	55 parts
	Styrene	10 parts
15	n-Butyl acrylate	9 parts
	2-Hydroxyethyl acrylate	5 parts
	Methacrylic acid	1 part

[0050]

Next, the reaction vessel described above was maintained at 80°C in an inside thereof, and 20.5 parts of the following monomer mixture (2) and 4 parts of 3% ammonium persulfate were added drop by drop to the reaction vessel at the same time in 1.5 hours. After finishing addition, the solution was aged for one hour and then filtered through a nylon cloth of 200 mesh at 30°C. Deionized water was further added thereto, and the pH was controlled to 7.5 with N,N-dimethylaminoethanol, whereby obtained was an acrylic resin aqueous dispersion (c-1) having an average particle diameter of 0.1  $\mu\text{m}$ , a Tg (glass transition temperature) of 46°C, and a non-volatile content of 20%.

## Monomer mixture (2)

	Methyl methacrylate	5 parts
30	n-Butyl acrylate	7 parts
	2-Ethylhexyl acrylate	5 parts
	Methacrylic acid	3 parts
	"Newcol 707SF"	0.5 part

[0051]

Synthetic Example 5: synthesis of an acrylic resin aqueous solution (c-2)

A reaction vessel was charged with 60 parts of ethylene glycol monobutyl ether and 15 parts of isobutyl alcohol and heated to 115°C in nitrogen flow. After the temperature reached 115°C, added in one hour were 26 parts of n-butyl acrylate, 47 parts of methyl methacrylate, 10 parts of styrene, 10 parts of 2-hydroxyethyl methacrylate, 6 parts of acrylic acid, and the mixture of one part of azobisisobutyronitrile and 5 parts of ethylene glycol monobutyl ether. The solution was aged for 30 minutes and then filtered through a nylon cloth of 200 mesh at 50°C to obtain a reaction product solution having a viscosity of Z<sub>4</sub> (Gardner bubble viscometer) and a non-volatile content of 55%. The reaction product (solid matter) had an acid value of 47 mg KOH/g and a T<sub>g</sub> of 40°C. The reaction product solution was neutralized with dimethylaminoethanol in an equivalence, and deionized water was further added, whereby an acrylic resin aqueous solution (c-2) having a non-volatile content of 50% was obtained.

[0052]

Mixed were 275 parts of the acrylic resin aqueous dispersion (c-1) having a non-volatile content of 20% described above, 40 parts of the acrylic resin aqueous solution (c-2) having a non-volatile content of 50% described above, 25 parts of "Cymel 350" (trade name, melamine resin, manufactured by Mitsui Cytec Co., Ltd.), 20 parts of "Aluminum Paste AW-500B" (trade name, metallic pigment, manufactured by Asahi Kasei Metals Co., Ltd.), 20 parts of ethylene glycol monobutyl ether, and 253 parts of deionized water. Then, added thereto was "Thixol K-130B" (trade name, anti-sagging agent, manufactured by Kyoeisha Chemical Co., Ltd.) to control the viscosity so that it was 300 mPa·s (millipascal-second) with a B type viscometer (rotation speed of rotor: 6 rpm), whereby obtained was a coating composition (C-1) for a water-based colored base coat having a non-volatile content of about 19%.

[0053]

Examples 1 to 14 and Comparative Examples 1 to 3

An epoxy base cationically electrodepositable coating composition was electrodepositably applied on a dull steel plate having a thickness of 0.8

mm which was subjected to zinc phosphate chemical conversion treatment so that the dried coating film thickness was about 20  $\mu\text{m}$ . The coating film was baked at 170°C for 20 minutes and then rubbed with a sand paper of #400, and it was wiped with petroleum benzine for degreasing. Then, an intermediate coating surfacer for automobiles was applied thereon by means of an air spray so that the dried film thickness was about 25  $\mu\text{m}$ , and it was baked at 140°C for 30 minutes and then wet-rubbed with a sand paper of #400. It was drained and dried, followed by wiping with petroleum benzine for degreasing, whereby a material for testing was prepared.

10 [0054]

Then, the coating composition (C-1) for a water-based colored base coat obtained in the preparation example described above was applied on this material so that the film thickness was 20  $\mu\text{m}$ , and it was dried at 80°C for 5 minutes. Then, the respective curing compositions described above which were controlled in a viscosity (viscosity: 30 seconds/Ford cup #4/20°C) were applied on the coated face thereof so that the film thickness was 40  $\mu\text{m}$  in terms of a cured coating film thickness, and both coating films were cured by heating at 140°C for 30 minutes.

[0055]

20 The coated test plates thus obtained were evaluated for a finish, coloring of the coating films, and a coating film hardness according to the following criteria.

[0056]

Finish: visually judged according to the following criteria.

- 25           ○ : smoothness, gloss, and sharpness are good, and nothing abnormal is observed
- Δ : any of smoothness, gloss, and sharpness is a little inferior
- X : any of smoothness, gloss, and sharpness is markedly inferior

[0057]

30 Coloring of the coating films: a coloring degree of the coating film was visually evaluated. In the tables, the term "none" shows that coloring is not observed and is good, and the term "brown" shows that the coating film is colored brown and coloring is inferior.

[0058]

Coating film hardness: a Knoop hardness (20°C) of the coated face on the coated test plate was measured.

[0059]

5 [Table 3]

Table 2

Example No.	Example								
	1	2	3	4	5	6	7	8	9
Kind of curing composition	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
Finish	O	O	O	O	O	O	O	O	O
Coloring	None	None	None	None	None	None	None	None	None
Knoop hardness	25	25	26	24	26	20	19	18	19

[0060]

10 [Table 4]

Table 2 (continued)

Example No.	Example					Comparative Example		
	10	11	12	13	14	1	2	3
Kind of curing composition	A-10	A-11	A-12	A-13	A-14	B-1	B-2	B-3
Finish	O	O	O	O	O	Uncured	O	Uncured
Coloring	None	None	None	None	None	None	Brown	None
Knoop hardness	10	14	9	7	5	—	26	—

[0061]

15 [Effect of the invention]

As can be found from the examples, according to the production method for a cured coating film of the present invention, a coating film which is not colored in baking and has good characteristics such as a hardness and a finish is obtained as well in coating by wet-on-wet, and it is very useful in terms of a shortening of steps and a grant of a design.

20

[0062]

According to the method for forming a cured coating film of the present invention, a curing composition on a top layer shows a good curing property in a wet-on-wet coating even when a lower layer comprises a

5 water-based color coating composition.



[Document Name] Abstract

[Abstract]

[Subject]

The present invention provides a method capable of forming a cured coating film which is excellent in curing property at a relatively low curing temperature and excellent in hardness and finish in a wet-on-wet coating step.

[Means for Solution]

A method for forming a cured coating film, characterized by applying, on an uncured thermosetting colored layer, a curing composition comprising:

(A) a polymerizable cyclic structure-containing component comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one  
5 polymerizable cyclic structure in a molecule and

(B) 0.01 to 2 parts by weight of a metal triflate per 100 parts by weight of the above component (A),  
wherein the above polymerizable cyclic structure-containing component (A) has  
10 a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average and then baking it .

[Selected Drawing]

None

**Certified - Additional Information**

Patent Application Number : Patent Application No. 2001-66440  
Reception Number : 50100335554  
Document Name : Patent Application  
Person in Charge : Masanori Kamata 8045  
Date of Executed : March 15, 2001

**<Certified Information - Additional Information>**

Date of Filing : March 9, 2001

[Name of Document] Voluntary Amendment

[Submitted to] Commissioner, Patent Office

[Indication of the Case]

[Application Number] Patent Application No. 2001-66440

[Person Making Amendment]

[Identification Number] 000001409

[Name] Kansai Paint Co., Ltd.

[Representative] Tamotsu SHIRAIWA

[Voluntary Amendment 1]

[Name of Document to be Amended] Patent Application

[Item to be Amended] Priority Claim Based on Prior Application

[Means of Amendment] Alteration

[Content of Amendment]

[Priority Claim Based on Prior Application]

[Application Number] Patent Application No. 2001-31763

[Date of Filing] February 8, 2001

[Proofing] Required

**Certified - Additional Information**

Patent Application Number : Patent Application No. 2001-66440  
Reception Number : 50101676138  
Document Name : Voluntary Amendment  
Person in Charge : Masanori Kamata 8045  
Date of Executed : November 21, 2001

**<Certified Information - Additional Information>**

Date of Filing : November 14, 2001

**Information of Applicant's History**

Identification Number : 000001409

1. Date of Changed : August 9, 1990

Reason of Changed : New Registration

Address : 33-1, Kanzaki-cho, Amagasaki-shi, Hyogo-ken

Company Name : Kansai Paint Co., Ltd.